# Synthesis of Poly(*m*-phenyleneisophthalamide) by Solid-state Polycondensation of Isophthalic Acid with *m*-Phenylenediamine

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**INTRODUCTION** Super engineering plastics are currently receiving considerable attention for their applications in the aerospace, automotive, electronic, and related markets. Aromatic polyamides (aramids), such as poly(m-phenyeleneisophthalamide) and poly(p-phenyleneterephthalamide), are important in the commercial fiber industry because of their high tensile strength and good flame resistance.1-8 There have recently been progresses in many applications based on highperformance aromatic polyamides, such as optoelectronic application.<sup>9-11</sup> The synthesis of aramids is normally achieved by the solution or interfacial polycondensation of aromatic diacid chlorides with aromatic diamines due to the lower reactivity of the aromatic amines compared to aliphatic amines and their high melting temperatures. From the standpoint of green chemistry, the direct synthesis of aramids from aromatic dicarboxylic acids and aromatic diamines without using any solvents and toxic chemicals is becoming increasingly important and more straightforward, being an environmentally benign transformation. However, no report on the synthesis of aramids using a solid-state polymerization process has been published except for our recent paper.<sup>12</sup> We reported the direct synthesis of aramids by the solid-state polvcondensation of aromatic dicarboxylic acids and aromatic diamines containing ether linkages which increased the mobility of the polymer chains, and decreased the glass transition temperatures  $(T_{\rm e}s)$  and melting points  $(T_{\rm m}s)$  of the resulting aramids.<sup>12</sup> The polycondensation under a nitrogen atmosphere proceeded in the melt state during the first step of the oligomer formation and then in the solid state to yield the desired aramids with high molecular weights. These findings suggested that other aramids with high melting points could be prepared without decomposition by the solid-state polycondensation method at high temperature. The next challenging target of aramids is the synthesis of poly(*m*-phenyeleneisophthalamide) (trade name: Nomex), which has high  $T_{\rm g}$  and  $T_{\rm m}$  values. Herein, we report the direct synthesis of poly(*m*phenyeleneisophthalamide) by the solid-state polycondensation of isophthalic acid with *m*-phenylenediamine. The optimization of the reaction conditions for the oligomerization and polymerization are described. No catalysts and plasticizers were used in the polycondensation to produce the pure poly(*m*-phenyeleneisophthalamide).

#### **RESULTS AND DISCUSSION**

Recently, Lange and coauthors investigated the thermal condensation of carboxylic acids with amines in the presence of molecular sieves, and found that aliphatic carboxylic acids smoothly reacted with primary and secondary aliphatic amines as well as aromatic ones at 160 °C for several hours.<sup>13</sup> On the other hand, the reaction of benzoic acid with an aromatic amine, such as aniline, gave around a 50% yield of benzanilide even at 160 °C for 24 h. Therefore, before the synthesis of the poly(*m*-phenyleneisophthalamide), the model reaction of benzoic acid (1) with *m*-phenylenediamine (2)was carried out in the melt state to investigate the feasibility of the direct synthesis of poly(*m*-phenyleneisophthalamide) (6) [Scheme 1(A)]. Considering the sublimation of 1, a small excess amount of 1 to 2 was used. These results are summarized in Table 1. All the reactions proceeded in homogeneous states and then N,N'-1,3-phenylenebis(benzamide) (3) was quantitatively obtained after 5 h at 240 °C. It was confirmed that 1 reacted with 2 in the range of 220-240 °C.

Based on the model reactions, the polycondensation of 2 with isophthalic acid (4) was carried out under various conditions in an argon atmosphere [Scheme 1(B)]. We first

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SCHEME 1 (A) Model reaction of 1 and 2. (B) Oligomerization and polymerization of 2 and 4.

investigated the appropriate conditions to obtain oligo (m-phenyleneisophthalamide) (5) by the direct polycondensation of 2 with 4 without any thermal decomposition and sublimation of the monomers. These results are summarized in Table 2. The synthesis of 5 was carried out at 240 °C, which was the optimized temperature based on the model reaction. When the reaction time was extended from 1 to 5 h at 240 °C, the inherent viscosity slightly increased. To accelerate the polycondensation, the reaction temperature was increased to 260 °C. The oligoaramid 5 with the inherent viscosity of 0.12 dL/g was obtained after 1 h (Run 4). Thus, the optimized condition for the oligomerization was determined to be 260 °C and 1 h. The structure of 5 was characterized by IR and <sup>1</sup>H NMR spectroscopies. The IR spectra showed the characteristic absorptions of the N-H and the C=O stretchings of the amino and amide carbonyl groups at 3266 and 1650 cm<sup>-1</sup>, respectively. Figure 1 shows a typical <sup>1</sup>H NMR spectrum of 5, in which the characteristic resonance of the amide protons at 10.4 ppm appears. For accurate assignments of the terminal groups of 5, model compounds, 3-(phenylcarbamoyl)benzoic acid (7) and N-(3-aminophenyl)benzamide (8) were synthesized and characterized as representatives for the carboxylic or amino terminal groups. As can be seen in Figure 1, the signals h and m correspond to the protons of the carboxylic acid and amine terminated amide protons, respectively. Thus, the

TABLE 1 Results of Model Reaction<sup>a</sup>

ratio of the carboxylic acid and amine terminated oligomers
can be estimated from the integral ratios of $\boldsymbol{h}$ and $\boldsymbol{m}.$ This
estimation is quite important because the ratio of $\boldsymbol{h}$ and $\boldsymbol{m}$ in
the oligomers should be $1.0\ to$ obtain high molecular weight
polymers in a subsequent postpolymerization process. The
feed ratio $R$ (=[2]/[4]) was then varied in such a way that
the ratio of h to m became 1.0. The results are summarized in
Table 3. In the case of $R = 1.2$ , the ratio of h to m became
${\sim}1.0,$ due to the sublimation of 2 during the heating process.

In the thermogravimetry (TG)/differential thermal analysis (DTA) analysis, the decomposition temperature of the oligomer was observed above 400  $^\circ\text{C}$  , and an endothermic peak corresponding to the melting point of the oligomers was observed around 408 °C (see Supporting Information, Fig. S1). Thus, the temperature for the postpolymerization was set at 350 °C [Scheme 1(B)]. In practice, the polymerization was carried out at 350 °C at a heating rate of 10 °C/ min after the oligomerization with R = 1.2 at 260 °C for 1 h. These results are summarized in Table 4. The inherent viscosity of 6 reached to 0.34 dL/g after the polycondensation for 80 min at 350 °C. By increasing the polymerization temperature to 360 °C, the inherent viscosity of 6 was improved to 0.37 dL/g. Then the polymerization was carried out under reduced pressure (0.05 Torr) at 370 °C to promote the polycondensation. Both the yield and inherent viscosity of the

TABLE 2 Results of Oligomeriza	ition
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Run	Conditions $T_1 (°C)/t_1$ (h)	Yield (%)
1	220/5	88
2	220/7	92
3	240/3	88
4	240/4	94
5	240/5	95
6	240/7	97

<sup>a</sup> Reactions were carried out with 3.0 mmol of 1 and 1.0 mmol of 2.

Run	Conditions $T_2$ (°C)/ $t_2$ (h)	Yield (%)	η <sub>inh</sub> (dL/g) <sup>b</sup>
1	240/1	88	0.099
2	240/3	82	0.11
3	240/5	82	0.12
4	260/1	96	0.12
5	260/3	96	0.12

 $^a$  Reactions were carried out with 1.0 mmol of **2** and 1.0 mmol of **4**.  $^b$  Inherent viscosities were measured at 30  $^\circ C$  in NMP at a concentration of 0.5 g/dL.



FIGURE 1 <sup>1</sup>H NMR spectra of (A) oligomer 5, (B) carboxylic terminal model 7, and (C) amino terminal model 8.

resulting aramid 6 were improved to 90% and 0.45 dL/g, respectively. To shorten the reaction time, the reaction temperature was increased to 380 °C, producing the aramid 6 with the inherent viscosity of 0.46 dL/g in 10 min. When the reaction time was extended to 30 min, a partially insoluble polymer in conc.  $H_2SO_4$  was formed, suggesting that side reactions such as crosslinking reactions and oxidation might occur. Finally, the polymerization was carried out at 400 °C for 1 min to produce the aramid 6 with an inherent viscosity of 0.55 dL/g. Number- and weight-average molecular weights ( $M_n$  and  $M_w$ ) values of 6 ( $\eta$  = 0.46 dL/g) determined by size exclusion chromatography (SEC) are 15,000

TABLE 3 Results of End Group Determination<sup>a</sup>

Run	Temp. (°C)/Time (h)	<i>R</i> <sup>b</sup>	Yield (%) <sup>c</sup>	η <sub>inh</sub> (dL/g) <sup>d</sup>	h/m <sup>e</sup>
1	260/1	1.0	96	0.12	6.2
2	260/1	1.1	96	0.13	1.2
3	260/1	1.2	99	0.12	1.1
4	260/1	1.3	98	0.11	0.6
5	260/1	1.5	99	0.099	0.2

<sup>a</sup> Reaction was carried out with 1.0 mmol scale under argon stream.

<sup>b</sup> The ratio of **2** to **4**.

<sup>c</sup> Isolated yield.

 $^{\rm d}$  Inherent viscosity was measured at 30°C in conc.  $H_2SO_4$  at a concentration of 0.5 g/dL.

<sup>e</sup> Determined by <sup>1</sup>H NMR.



and 34,000, respectively. From the <sup>1</sup>H NMR spectrum (Supporting Information, Fig. S2), the characteristic signals h and m for the terminal units, as seen in the oligomers (Fig. 1), almost disappeared, indicating the increase in the molecular weights of the aramid 6.

#### EXPERIMENTAL

## Materials

*m*-Phenylenediamine (2) was sublimated prior to use. Isophthalic acid (4) purchased from Tokyo Chemical Industry

#### **TABLE 4** Results of Polymerization

Run	Rª	Conditions T <sub>3</sub> (°C)/t <sub>3</sub> (min)	Yield (%) <sup>b</sup>	η <sub>inh</sub> (dL/g) <sup>c</sup>
1 <sup>d</sup>	1.2	350/80	81	0.34
2 <sup>d</sup>	1.2	360/80	80	0.37
3 <sup>e</sup>	1.2	370/360	90	0.45
4 <sup>e</sup>	1.2	380/10	87	0.46
5 <sup>e</sup>	1.2	400/1	94	0.55

<sup>a</sup> The molar ratio of 2 to 4.

<sup>b</sup> Isolated yield.

 $^{\rm c}$  Inherent viscosity was measured at 30  $^{\circ}\text{C}$  in conc.  $\text{H}_2\text{SO}_4$  at a concentration of 0.5 g/dL.

 $^{\rm d}$  The polymerization was carried out with 1.0 mmol scale under an argon atmosphere.

<sup>e</sup> The polymerization was carried out with 1.0 mmol scale under reduced pressure of 0.05 Torr.

was recrystallized from ethanol prior to use. Model materials, 3-(phenylcarbamoyl)benzoic acid (7) and *N*-(3-aminophenyl)benzamide (8) were synthesized according to the literatures.<sup>14,15</sup> The other reagents and solvents were commercially obtained and used as received.

#### Measurements

FTIR spectra were recorded on a Horiba FT-720 spectrometer. <sup>1</sup>H NMR spectra were recorded with a Bruker DPX300S spectrometer. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for TG.  $M_n$  and  $M_w$  values were determined by SEC, calibrated by standard polystyrene samples, on a JASCO PU-2080Plus system equipped with two polystyrene gel columns (TSKGELs; GMHHR-M). *N,N*-Dimethylformamide (DMF) containing 0.01 M LiBr was used as a solvent at a flow rate of 1.0 mL min<sup>-1</sup>.

#### Synthesis of *N*,*N*'-1,3-Phenylenebis(benzamide) (3)

Benzoic acid (1) (0.366 g, 3.0 mmol) and *m*-phenylenediamine (2) (0.108 g, 1.0 mmol) were placed to a Pyrex test tube (15 mL) equipped with argon gas inlet and outlet tubes. The mixture was heated with an oil bath at 240 °C under an argon atmosphere for 4 h, and then allowed to cool to room temperature. The solids were dissolved in DMF (3 mL), and the resulting solution was poured into a 1 wt % NaHCO<sub>3</sub> aqueous solution (300 mL) to remove the excess of benzoic acid. The precipitate was collected, dried *in vacuo* at 120 °C overnight. The yield of the model compound was 0.297 g (94%): m.p. 246–250 °C (lit. 239–240 °C). IR (KBr), v (cm<sup>-1</sup>): 3266 (-NH), 1650 (C=O). <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$ , ppm, 300 MHz): 10.3 (s, N—H, 2H), 8.36 (s, ArH, 1H), 8.02 (d, J = 6.9 MHz, rH, 4H), 7.67–7.47 (m, ArH, 8H), 7.36 (t, J = 9.0 MHz, ArH, 1H).

#### Synthesis of Oligo(*m*-phenyleneisophthalamide) (5)

In a 10-mL Pyrex tube equipped with a stirring bar and argon gas inlet and outlet tubes, the monomer **2** (1.0 mmol) and monomer **4** (1.0–1.5 mmol) were placed under a stream of argon. The mixture was gradually heated up to 260 °C with a heating mantle for 1 h, and then allowed to cool to room temperature. The solid was dissolved in conc.  $H_2SO_4$  (1.5 mL), and the solution was poured into water (300 mL). The solution was neutralized by NaHCO<sub>3</sub> (4.5 g). The oligomer was collected, and dried *in vacuo* at 120 °C for 1 day.

#### Synthesis of Poly(*m*-phenyleneisophthalamide) (6)

In a 15-mL Pyrex tube equipped with a stirring bar and argon gas inlet and outlet tubes, **4** (0.166 g, 1.0 mmol) and **2** (0.130 g, 1.2 mmol) were placed under a stream of argon. The mixture was heated with a heating mantle at 260 °C under an argon atmosphere for 1 h. The resulting oligomer was heated at 400 °C for 1 min under vacuum and then allowed to cool to room temperature. The solid was dissolved in conc. H<sub>2</sub>SO<sub>4</sub> (7 mL), and the solution was filtered through the glass filter 3G-3. Additional 3 mL of conc. H<sub>2</sub>SO<sub>4</sub> was added to wash the Pyrex tube and the filter. The combined conc. H<sub>2</sub>SO<sub>4</sub> solution was poured into water (300 mL) to precipitate the polymer, followed by neutralization with NaHCO<sub>3</sub> (30 g). The polymer was collected, and dried *in vacuo* at 120 °C for 1 day. The yield of polymer was 0.224 g (94%). IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3429 (—NH), 1658 (C=O). <sup>1</sup>H NMR

(DMSO- $d_6$ ,  $\delta$ , ppm, 40 °C): 10.4 (s, N—H, 1H), 8.03 (d, J = 8.7, ArH, 4H), 7.79 (d, J = 9.0, ArH, 4H), 7.51 (d, J = 8.4, ArH, 4H), 7.34 (t, J = 8.4, ArH, 1H), 7.08 (d, J = 9.0, ArH, 4H), 6.70 (dd, J = 8.3, 2.1, ArH, 2H), 6.60 (t, J = 2.7, ArH, 1H).

#### CONCLUSIONS

We directly synthesized poly(*m*-phenyleneisophthalamide) from isophthalic acid with *m*-phenylenediamine by a solid-state polycondensation. The model reactions between low nucleophilic *m*-phenylenediamine and benzoic acid quantitatively proceeded simply by heating to yield the desired aromatic diamide. When the feed ratio R (=[2]/[4]) was 1.2, the oligomer with equimolar carboxylic acid and amine terminal groups was obtained under the optimized conditions. Based on the optimized conditions, the polymerization was carried out at 400 °C for 1 min under reduced pressure after the oligomerization at 260 °C for 1 h. As a result, poly(*m*-phenyleneisophthalamide) with a maximum inherent viscosity of 0.55 dL/g could be obtained. This environmentally friendly method can be applied to the synthesis of aramids with high melting points that are currently produced via the thionyl-chloride-based method.

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